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(54) Alkaline Cell Container Having Interior Conductive Coating

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Canada

90°C 180°C

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ALKALINE CELL CONTAINER HAVING INTERIOR CONDUCTIVE COATING

ABSTRACT OF THE INVENTION

A coating for the interior of alkaline cells is provided, so that a coated cell container or can may have a cell depolarizer inserted into the can without scraping the coating off the interior surface in any substantial amounts. The coating includes carbon particles (and may include other conductive particles such as nickel, silver or graphite particles, carbon black or acetylene black) carried in a binder with a volatile carrier which will evaporate at room temperature. A hard conductive coating is formed after the volatile carrier has evaporated, which reduces the initial interior cell depolarizer/can interfacial resistance, and maintains it after storage at a lower level than that of uncoated cans. The coating composition is applied to the interior of the cans after they have been formed, by such steps as dipping, filling or spraying.

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CLAIMS:

1. For use in alkaline cells, a cathode container having a coating on at least the major portion of the interior surface thereof;

where the coating composition for said coating includes carbon particles carried in a binder with a volatile carrier;

where said carrier is such that it will evaporate at room temperature;

where said binder and carbon particles are such as to form a hard conductive coating over the surface onto which said coating composition has been applied, after said carrier has evaporated; and

where said hard coating is substantially impervious to alkaline electrolyte, and is electrically conductive;

whereby the contact resistance between said can and a cell depolarizer when tightly fitted thereinto is initially in the range of zero to 20 milliOhms when measured at room temperature, and after storage of at least one week said contact resistance increases only in the range of zero to four times the initial resistance.

2. The interior coated cathode container of claim 1, where said hard coating has substantially no tendency to swell in the presence of alkaline electrolyte.

3. The combination of claim 2, where the electrolyte is chosen from the group comprising potassium hydroxide and admixtures thereof with zinc oxide.

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4. The interior coated cathode container of claim 2, where the can has a plurality of inwardly directed ridges which extend vertically for substantially the entire height of the can, and which are spaced circumferentially around the can.

5. The interior coated cathode container of claim 1, where said binder is a nitrocellulose lacquer.

6. The interior coated cathode container of claim 1, where said coating composition has first been admixed with butylacetate.

7. The interior coated cathode container of claim 1, where said coating composition is a commercial composition sold as ECCOCOAT® 257.

8. The interior coated cathode container of claim 1, where said coating composition is a commercial composition sold as ELECTRODAG® 109.

9. The combination of claim 4, where the cell depolarizer is interference fit with at least the inside facing surfaces of said inwardly directed ridges.

10. The interior coated cathode container of claim 1, where said coating composition further includes, as a conductive component thereof, at least one of the group comprising nickel particles, silver particles, graphite particles, carbon black, and acetylene black.

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11. The interior coated cathode container of claim 1, where said coating composition includes methyl ethyl ketone as a diluent.

12. The combination of claim 1, where said container has a first coating or plating of nickel or nickel alloy on at least the interior surface thereof before said coating composition has been applied thereto.

13. A method of preparing an alkaline cell, at least to the stage where at least a portion of the cell depolarizer is inserted into a formed can with a coating composition which includes carbon particles carried in a binder with a volatile carrier;

permitting the volatile carrier to evaporate so as to leave a hard, conductive coating on the inside surface of said can, which coating is substantially impervious to alkaline electrolyte; and

placing into said can at least a portion of the cell depolarizer, so that, when placed, said at least a portion of said cell depolarizer is tightly fitted into said can.

14. The method of claim 13, where the coating composition is applied to at least the inside surface of the can by one of the following steps:

(a) dipping the can into a bath of coating composition

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and withdrawing it from the bath so as to leave a residue within the can;

(b) filling the can with coating composition and then spilling coating composition from the can so as to leave a residue within the can;

(c) spraying the interior of the can with coating composition at room temperature; or

(d) spraying the interior of the can with coating composition which has been pre-heated to 25 to 45° C.

15. The method of claim 14, followed by one of the following steps:

(e) allowing the volatile solvent to evaporate at room temperature for at least three hours; or

(f) allowing the volatile solvent to evaporate at a temperature of 50 - 90° C for at least 0.2 to 2 hours.

16. The method of claim 15, where said coating composition is admixed with butyl acetate in the range of composition:butyl acetate ratios of from 1:8 to 8:1.

17. The method of claim 13, where said coating composition further includes, as a conductive component thereof, at least one of the group comprising nickel particles, silver particles, graphite particles, carbon black and acetylene black.

18. The method of claim 13, where said coating composition includes methyl ethyl ketone as a diluent.

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The method of claim 13, where said formed can has a first coating or plating of nickel or nickel alloy on at least the interior surface thereof before said coating composition is applied.

20. The method of claim 14, where the coating composition is applied to the inside surface of the can when the can has first been pre-heated to a temperature of between 50 to 150° C;

where the coating is sprayed into the can at a temperature of between 15 to 45° C; and where the can is then allowed to air dry at room temperature for at least 15 seconds.

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FIELD OF THE INVENTION:

This invention relates to alkaline cells, and particularly to containers or cathode cans into which alkaline cells are assembled. This invention finds its principal use in cylindrical alkaline dry cells which have a substantial axial length as compared to their diameter. Such cells bear the general designations, as to their size, ranging from "AAA" as the smallest up to "D" as the largest.

BACKGROUND OF THE INVENTION:

One of the principal causes for the loss of apparent energy capacity of alkaline dry cells, once they have been manufactured and are placed in storage such as shipping inventory or on merchants' shelves for purchase by the consuming public, -- and indeed, abusive storage by the consumer such as in the heated interior of automobiles, and/or for long periods of time -- has been the increase of contact resistance between the material of the cathode within the cell and the container in which the cell has been assembled. This increase in contact resistance may be manifested by a reduced on load terminal voltage, faster reduction to a cut-off voltage, or reduced photoflash capabilities. It occurs because of the fact that the material of the cell container or can -- usually nickel plated steel -- -- is subject to corrosion, particularly in the presence of alkaline electrolyte. Of course, the electrolyte most often used in such cells is potassium hydroxide, which may have additional amounts of zinc oxide admixed thereto.

One approach to overcome the problem of internal corrosion apart from nickel plating, is to provide yet an

additional conductive coating on the interior surface of the can, which coating may then provide a low resistance interface between the cathode material and the can, while at the same time protecting the material of the can from corrosion.

The decision to provide an electrically conductive layer on the interior surface of the cathode can has prompted a review of the prior art, generally in respect of conductive coatings, and particularly for any art which may relate to the presence of a conductive coating on the interior surface of a cathode can, with the following results:

WHITNEY et al in U.S. Patent 2,806,078, issued September 10, 1957, teach a cylindrical dry cell battery in which the inner can wall and the adjacent anode surface are coated by a layer of electrically conductive "grease" -- which is a dimethyl siloxane filled with silica. This "grease" provides a contact between the anode and the can. However, so as to uniformly distribute the coating on the inner surface of the can, the can is subjected to radio frequency heating.

KILDUFF in United States Patent 3,751,301 issued August 7, 1973, has provided a non-corrodible electrically conductive underlayer to a metal support body, which is sufficient to prevent the formation of an interfacial resistance barrier between the metal support body and a subsequently applied coating. This electrically conductive material is applied to the metal support body in admixture with a thermosetting resin. The thermosetting resin may be a water emulsifiable epoxy resin, and is admixed with a conductive material such as carbon or graphite. After curing, a second coating which consists of a mixture of lead dioxide and a thermosetting binder is applied, and the

structure is then suitable for use as a reserve battery electrode in an acid system.

KUWAZAKI et al in United States patent 3,764,382, issued October 9, 1973, teach an inside-out primary dry cell in which the metallic container is coated with a conductive mixture of a thermoplastic resin and graphite or acetylene black. This cell is said to have good performance characteristics, particularly when operating in a deep discharge mode to a high current load.

None of the above United States patents have, however, provided a suitable coating for the interior surface of alkaline cells, particularly where the coating must provide a high conductivity -- i.e., low resistance -- current path between the cathode material of the cell and the cell container, so as to establish a conducting circuit through the cell; while, at the same time, also providing a coating which will withstand the rigors of manufacturing steps where the assembly of a cell is fully automated and is accomplished at very high speeds such that any one assembly step may only take fractions of a second. Still further, it is not in the least desirable to use any conductive coating on the interior surface of a cathode can which would occupy any significant volume, thereby reducing the volume within the can which is available for active electrode or electrolyte material.

Japanese Patent Publication 48361-1983, published March 22, 1983 by SHINODA et al, teaches an alkaline dry cell battery where the interior surface of the cathode can is coated with a conductive coating which comprises polyvinyl isobutyl ether and carbon -- which may be graphite or flake shaped graphite, and/or acetylene black. However, SHINODA et al, while claiming to

provide their conductive coating on the interior surface of the cathode can, which results in alkaline cells having high short circuit currents even following storage of six to twelve months, have provided a coating which is sticky to the touch, and which has rubber elasticity. This suggests, therefore, that the electrically conductive layer which is formed on the interior surface of the can, may also be relatively soft so that, when the cathode material is loaded into the can, especially where the cathode material is preformed extruded or compacted pellets or slugs, the coating on the interior surface of the can may be scraped off and thereby be of no significant value.

Because of that problem, SHINODA et al teach that their cathode is a blend of manganese dioxide powder and graphite, which is packed into the can. However, that requires a step which takes a significant amount of time during the manufacturing process, and which cannot ensure consistant and repeatable characteristics from cell to cell of a batch of many cells that are manufactured under high speed conditions. Moreover, SHINODA et al require that a further manufacturing step be taken, by heating the container and thereby dissolving the material of the electrically conductive layer after the cathode blend has been incorporated into the cell. This step is taken so as to fill the uneven spaces on the inner wall of the container and thereby enhance the electrical contact between the container and the cathode blend.

The present invention, on the other hand, has none of the shortcomings of SHINODA et al. In particular, the present invention provides a coating composition which achieves essentially the same results -- that is, significantly reduced

...rosion of the steel can, which may be nickel plated as well -- and thereby increased short circuit performance, with much lower cathode/can interface voltage drop due to contact resistance at that interface. Moreover, the present invention provides a coating composition, as well as a cell can or cathode container having a coating on its interior surface, where the coating is hard and not subject to scraping. Thus, the coating will not lose its physical placement within the can and thereby its effectiveness after the cell has been assembled during manufacturing; and, as well, the coating which results according to the present invention is substantially impervious to alkaline electrolyte, while being at the same time electrically conductive.

Thus, especially when the cell depolarizer or cathode is placed into the can and is tightly fitted therein to -- such as by an interference fit -- the contact resistance between the can and the cell depolarizer may be initially in the range of from zero to twenty milliOhms when measured at room temperature, and after storage (even under extreme conditions of temperature) the contact resistance between the can and the cell depolarizer -- cathode -- may increase only in the range of from zero to four times the initial resistance. Alternative methods of placing the cell depolarizer in a can, apart from pressing depolarizer pellets which are in interference fit with the can, but which will ultimately result in the same characteristics as discussed immediately above include placing loose fitting pellets into the can and then recompacting them by placing a rod into the central portion of the cathode pellets and then applying compacting pressure against the pellets so as to recompact them and spread

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the compacted cathode material outwardly; or extruding the cathode material around and past a rod placed in the centre of the can, so as to ensure that the length of the can which is intended to be filled with cathode or cell depolarizer material is substantially completely filled with that material; or other means where, in any event, a substantially rigid material is placed into the can and, when placed, is tightly fitted within the can.

Examples of cells exhibiting improved contact resistance characteristics as discussed above, and improved operating characteristics such as higher short circuit currents and better photoflash capacities, will be discussed hereafter.

It is a characteristic of the present invention that the hard coating, once formed on the interior surface of the cathode can, has substantially no tendency to swell in the presence of alkaline electrolyte. Therefore, efficient employment of the interior volume capacity of the can may be achieved, having the most advantageous mix of volumes of the positive and negative electrode materials, liquid electrolyte, current collector, separator, and so on, while at the same time allowing for any internal gassing or swelling of the separator, without having to otherwise accommodate swelling of the coating material.

It has been found that the present invention also is particularly useful in cell designs which accommodate tightly fitted cathode pellets, that the can may have a plurality of inwardly directed ridges which extend vertically for substantially the entire height of the can, and which are spaced circumferentially around the can. Those ridges tend to secure the cathode or cell depolarizer within the can more efficiently, and

at the same time provide for firm contact between the cell depolarizer and the can and thereby provide a good electron path. At the same time, some void volume is permitted for occupation by electrolyte.

It is recognized by the present invention that the coating compositions that are particularly intended for use in keeping with this invention demonstrate substantially no tensile strength. Therefore, it is a characteristic of the present invention that the cell container or can is first formed such as by being stamped or drawn from material such as nickel plated steel and thereafter the coating is applied to the interior surface of the formed can by applying coating composition and permitting it to cure, as discussed hereafter.

It has been found, rather unexpectedly, that certain commercially available carbon based lacquers which are said to be essentially semi-conductive, and are intended for uses entirely differently than the present purposes, are suitable for the purposes of the present invention. They include a product marketed by W.R. Grace & Co., in association with the trade mark ECCOCOAT 257, and another product marketed by Acheson Industries, Inc. in association with the trade mark ELECTRODAG 109.

Generally, however, it can be said that the coating composition for use in the present invention is one which includes carbon particles carried in a binder with a volatile carrier, where the carrier is such that it will evaporate at room temperature, where the binder is such as to form a hard coating over a surface onto which it has been applied after the carrier has evaporated, and where the hard coating is substantially impervious to alkaline electrolyte and is electrically

conductive. The coating composition may also include, or a conductive component thereof, nickel particles, silver particles, graphite particles, carbon black, acetylene black, or any or all of them.

Moreover, the binder may be such as a nitrocellulose lacquer or other fortified organic polymer; and the coating composition may first be admixed with butyl acetate before it is applied, or it may include methyl ethyl ketone as a diluent.

BRIEF DESCRIPTION OF THE DRAWINGS:

The above features and advantages of the present invention are more fully described hereafter, and a typical preferred embodiment is illustrated in the accompanying drawings, in which:

Figure 1 is an exemplary axial cross section of a typical alkaline cell according to the present invention at a stage during its manufacture when the cell depolarizer has been inserted into the container; and

Figure 2 is an exemplary diametric cross section of a similar cell to that of Figure 1.

DESCRIPTION OF THE PREFERRED EMBODIMENTS:

As noted above, it is the principal purpose of this invention to provide a cathode container having a coating on at least the major portion of its interior surface, whereby the operating characteristics of the cell have experienced no significant deterioration following storage, either at the time when the cell goes into the hands of the consumer who has purchased it, or later. Storage may be as little as one or two

weeks or as much as many months, and may occur at room temperature or at elevated or depressed temperatures, and occurs due to the necessity to move cells into the manufacturer's inventory, and then into the distribution channels, onto the merchants' shelves for purchase by the consumer, and in the hands of the consumer. Significant periods of time may pass during all of those stages.

The present invention also provides the steps for the method of preparing an alkaline cell, at least to the stage where at least a portion of the cell depolarizer is inserted into the cathode can of the cell.

Referring to Figures 1 and 2, a typical but exemplary configuration is shown of a portion of a cell 10, which comprises a container or can 12 which may be formed of such material as steel, and may be stamped or drawn from that material. The material of the can 12 may be plated with nickel or nickel alloy, at least on the interior surface thereof.

Over the interior surface of the can 12 there is a coating 14 which is in keeping with the present invention, and is described in more detail hereafter. Also within the cell 10 is a cell depolarizer 16 which may have an opening 18 in its centre for the insertion of the other electrode material, a current collector, and so on. The precise details of the assembly of the cell are not relevant to the present invention.

The can 12 may be formed with a plurality of ridges 20, each of which extends vertically for substantially the entire height of the cell, and the ridges are spaced circumferentially around the can. [For purposes of the present discussion, four ridges are shown, but there may be as few as three and as many as

twelve or more.) In a "D" size cell, the ridges may have an inwardly extending height of about 0.032 inches.

As noted, the coating composition of the present invention has a carrier which will evaporate at room temperature. When the volatile carrier has evaporated, a hard coating remains, and that coating has the general characteristic of a matrix which remains and is firmly bonded to the material of the can. The conductive component of the coating composition is securely retained in place in the interstices of the matrix; so that a contiguous, conductive, hard, coating is formed, which coating is substantially impervious to the alkaline electrolyte -- which may be potassium hydroxide and may have zinc oxide admixed thereto -- and which has no tendency to swell in the presence of the alkaline electrolyte.

However, because the hard coating has no tensile strength, it must be put in place after the container or can is formed. That may be accomplished, for example, by any of the following steps:

(a) the can may be dipped into a bath of coating composition and withdrawn therefrom, so as to leave a residue of coating composition within the can;

(b) the can may be filled with coating composition and then spilled, so as to leave a residue of the coating composition within the can; or

(c) the interior of the can may be sprayed with the coating composition, and any residue may be permitted to run out from the can.

Indeed, in certain circumstances, the interior of the can may be brushed with the coating composition.

Thereafter, the volatile solvent of the coating composition is permitted to evaporate, such as at room temperature for at least three hours, or at an elevated temperature of 55 to 90° C for at least 0.2 to 2 hours.

Alternative methods of applying the coating composition to the interior of the can include preheating the coating composition to 25 to 45° C, and spraying it into the can. In yet another coating method, the cans themselves may be preheated to between 50 and 150° C, with the coating composition being between 15 and 45° C. The coating composition is then sprayed into the cans, which are then air dried at room temperature for at least 15 seconds. During that period of time, the volatile solvent is driven off, and the can cools down at least to some extent.

The initial contact resistance between the can and the cell depolarizer 16, may be measured and may be found to be initially in the range of zero (that is, below the measurement sensitivity of the instrument being used) up to about 20 milliohms -- usually in the range less than 4 milliohms. Then, following storage under various conditions, such as from two weeks to fifty-two weeks at room temperature, two weeks at 55° C, or one week at 71° C, tests have shown that the contact resistance between the can and the cell depolarizer may have increased only in the range of from zero -- that is, not at all -- to four times the initial resistance when the cell was first formed. Thus, even after storage under adverse conditions, the contact resistance between the can and the cell depolarizer may be in the range of from substantially zero up to 80 milliohms at the worst. Similar uncoated cans -- but having a nickel plating on their interior surface -- have been tested under similar

conditions using identical testing equipment, after they were stored in exactly the same conditions, and have demonstrated increases in contact resistance on storage up to 200 milliOhms or more.

The thickness of the hard coating, once it has been placed and cured, may be as little as 0.0002 to 0.003 inches, typically 0.0004 to 0.001 inches. Such thin coatings have no significant effect on the decrease of the internal volume of the can; and since the coating shows no tendency to swell in the presence of alkaline electrolyte, there is no necessity for permitting additional volume within the container to accommodate such swelling. This permits the addition of more active material to the cell, thereby giving it longer life and even better storage characteristics.

The coating composition may be admixed with butyl acetate over a range of ratios of composition to butyl acetate of from 1:8 to 8:1. The choice of the mixing ratio depends on such characteristics as the initial characteristics of the coating composition as it has been manufactured or purchased, the speed of the manufacturing line and the method in which the coating composition will be applied to the interior surfaces of the cans, the temperature and rate at which the coating composition will be cured, and the size of the cell container (large or small).

Representative test results have demonstrated the following:

In one series of tests, control (i.e., uncoated) cells stored for six weeks at room temperature have shown an average increase in internal cathode/can contact resistance of 40 milliohms, which would result in a loss of 16 millivolts of

terminal voltage at a cell current into a relatively heavy load of 400 milliAmps. Coated cells, according to the present invention, and stored under the same conditions, showed an average increase of internal resistance of zero, and therefore no measurable loss in terminal voltage of the cell even into a 400 milliAmp load.

Likewise, control cells stored for two weeks at 55°C showed an average increase of internal resistance of 85 milliOhms, for a loss of terminal voltage of 34 millivolts into a 400 milliAmp load; whereas cells having an internal coating according to the present invention, and stored under the same conditions, showed an average increase in internal resistance of 4 milliOhms for a loss of terminal voltage of 1.6 millivolts into a 400 milliAmp load.

Other cells in sizes ranging from "AA" to "D", following storage for two weeks at 55°C, showed improvements in operating characteristics of cutoff voltage into various loads of up to 22%. Moreover, "AA" cells into a photoflash load showed improvements of 20% in terms of the number of flashes permitted, and 50% recovery time after the fifth flash, as compared to control cells.

The short circuit current of various cells were tested following differing storage conditions, against control cells. For example, best "D" cells showed no significant change of average short circuit current for cells according to this invention, after various storage conditions; so that cells stored at 55° C for two weeks, and an average short circuit current of 19.3 milliAmps, and cells stored at 71° C for one week had an average short circuit current of 19.4 milliAmps. Control

"D" cells showed a decrease of average short circuit current to 14.0 milliAmps for cells stored at 55° C for two weeks, and to 11.6 milliAmps for cells stored at 71° C for one week. "C" cells showed an average short circuit current of 14.4 milliAmps for cells stored at 55°C for two weeks; whereas the control cells dropped from 9.9 milliAmps initially to 8.3 milliAmps following storage. Substantially similiar results were obtained with "AA" cells.

The benefits of a hard coating which is impervious to alkaline electrolyte, and which improves the internal contact resistance of alkaline cells, have been fully discussed and clearly demonstrated by the above. The fact that the coating is a hard coating, precludes the possibility that the coating will be scraped in any substantial amounts into the bottom of the cell container when the cell depolarizer is inserted into it; and it also provides for much easier can storage where the cans may be stored in bulk containers without having to worry about the possibility of the coating on the inside of the cans drooping or running during storage. Various specific examples of coating composition have been provided, but it is shown that in all events the coating composition includes at least carbon particles and may include additional conductive particles, carried in a binder with a volatile carrier which will evaporate at room temperature.

In general, given that the contents of an alkaline cell -- that is, the amount of cathode material, anode material, electrolyte, the separators, and the cell construction including the can material, the seal, and the method of the cell construction -- are constant between cells according to this

invention and control cells or cells that are presently available, with the only difference being the addition of the coating composition and the presence of the hard coating on the interior surface of the cathode container in keeping with this invention. It follows that for the most part the total capacity in milliAmp-hours of cells according to this invention and ordinary cells is essentially the same. However, cells according to this invention have shown a higher initial current, higher terminal voltage on load, with a higher short circuit current. The cells provide a higher average current into a constant resistance, although perhaps for a slightly shorter period of time due to the maximum milliAmp hour capacity of the cell; but they provide better service hours for cells working into a constant current load, and a much shorter recharge time for cells operating with a photoflash load.

Several examples of cell testing have been described and discussed, and a typical construction which is exemplary and not intended to limit the present invention, has been indicated. The scope of the present invention is defined by the appended claims.

90° 180°

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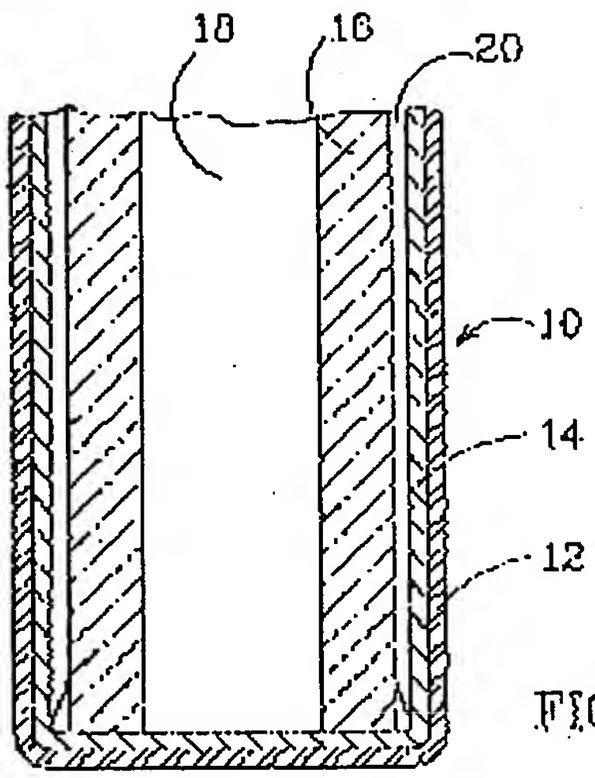

FIG. 1

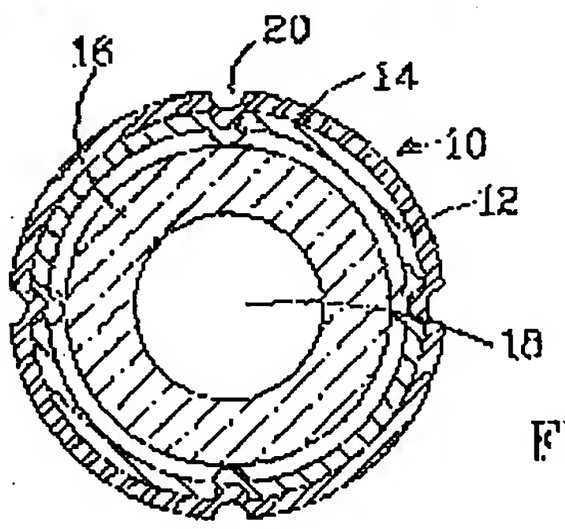

FIG. 2